

# PATENT SPECIFICATION

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## DRAWINGS ATTACHED

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## (54) IMPROVEMENTS RELATING TO ADHESION

(71) We, W. R. GRACE & Co., a Corporation organized and existing under the laws of the State of Connecticut, United States of America of 7 Hanover Square, New York 5, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to the use of thermally activatable adhesive compositions in joining two articles.

In one aspect the invention consists in a method for effecting adhesion between two articles which comprises interposing between them, and in contact with a surface of each, a thermally activatable adhesive composition containing carbon particles, and subjecting the assembly to the action of a high frequency alternating magnetic field until the adhesive composition has been heated sufficiently to become activated.

The adhesive composition may contain a thermoplastic hot melt, or thermosetting synthetic resin or a precursor thereof, e.g. a polymerisable monomer or low polymer. A thermoplastic or hot melt composition may be plasticised or unplasticised. Examples of thermoplastic materials are olefin polymers, especially polyethylene, polypropylene, ethylene/propylene copolymers, and polystyrene, and vinyl polymers, e.g. plasticised polyvinyl chloride, polyvinyl acetate, and polyvinyl acetals such as the butyral. Examples of hot melt compositions include the high molecular weight linear polyamides. Thermosetting resin compositions include the cross-linking polyesters,

as well as phenol-formaldehyde, urea-formaldehyde, and melamine-formaldehyde resins. The composition may if desired contain two or more components, e.g. a melamine- or phenol-formaldehyde resin and a polyvinyl acetal.

The carbon particles may be of graphite or amorphous carbon, e.g. carbon black. Graphite may be in the form of roughly spherical particles or thin platelets of various sizes. Such spherical particles usually have a diameter of 100 microns or less, and may be as small as 30 microns or less. Amorphous carbon is obtainable in a wide range of particle sizes, the particles again being roughly spherical.

The particles need not be composed wholly of carbon. For example the carbon may be in the form of a coating on an inert electrically non-conducting support, such for example as very fine glass beads. Such material may be obtained by treating the particles of the support, which will usually be roughly spherical, with a colloidal suspension of graphite in water or some other liquid, which may advantageously contain also a non-conducting binder resin of known type. Such support particles may have a diameter of 20—850 microns. Composite particles of this kind are included within the term "carbon particles" as used herein.

While there is no critical upper limit to the size of the individual carbon particles (which will depend on such factors as their influence on the mechanical strength of the final adhesive layer, and the desired thickness thereof) the normal upper limit of the average diameter may be taken as approximately 1 mm, and in most circumstances about 400—500 microns. When the particles in the composition are



- quite separate from each other, the lower limit is set by the fact that their thickness must be at least twice the effective depth of current penetration. However if the concentration and distribution of the carbon particles is such that a number of them together form an electrically conducting network, smaller particles can be used. The depth of current penetration is determined by various factors including the frequency and strength of the alternating magnetic field, and thus no lower limit for particle size can be given that is valid in all circumstances. As a general rule however it may be taken that, unless an electrically conducting network of particles is formed as described above, the particle size should not be lower than 30 microns and will preferably be about 50-200 microns, and especially 75-150 microns. Even when a conducting network is formed, the above size ranges will usually be found to be most suitable. Other things being equal, the larger the particles the more rapidly will the adhesive reach its activation temperature.
- 5 The carbon particles are preferably randomly distributed in the adhesive (or as nearly as possible randomly distributed bearing in mind that the particles may settle somewhat before the heating takes place).
- 10 The weight ratio of carbon particles to adhesive material may be varied over a wide range, e.g. from 5:95 to 80:20, and will be chosen with regard to the particular requirements of each case. Naturally the higher the ratio the more rapidly will the composition be heated by a field of any given frequency and strength. On the other hand the use of a high proportion of particles will often increase the stiffness of the final adhesive layer, which will not always be desirable; also it may decrease the wetting power of the adhesive for the surfaces to be joined, and may also decrease the cohesive strength of the adhesive layer, especially when the proportion is towards the upper end of the range. The importance of these effects will vary a good deal with the nature of the adhesive composition. Thus, compositions comprising highly crystalline polymers, e.g. high density polyethylene, are particularly sensitive, since the particles tend to be concentrated in the amorphous parts of the polymer layer, so that very high local concentrations arise even when the overall loading is comparatively low.
- 15 When small particles are used, e.g. particles of diameter below 30 microns, so that it becomes necessary to rely on the formation of an electrically conductive network as already described, the concentration of the particles should be sufficient to give a suitable bulk volume resistivity, generally between  $10^4$  and  $5 \times 10^4$  ohm-cm. for the best results.
- 20 The invention can be applied to the joining articles whose surfaces are of different types of polymer, e.g. reinforced or unreinforced thermoplastic or thermoset resins or rubber, or any combination of these. In choosing a suitable adhesive for any particular combination of surface materials, the ordinary knowledge of the art of adhesion will of course be made use of. Any number of surfaces may be joined together at the same time provided that a magnetic field of suitable coverage can be generated to heat each layer of adhesive. Thus laminates of several articles can be made if desired.
- 25 The invention is of particular value in the sealing of closures onto plastics containers, particularly plastics bottles. The conventional method of sealing bottles with a crown cap is unsuitable for closing many plastics bottles, particularly those of polyvinyl chloride, because high proportion of bottles are damaged by the pressure necessary for the closure. The method of the present invention makes it possible to seal a cap to a plastics bottle without distorting the bottle, and at a high speed so that the operation can keep pace with the high-speed filling operation which is the preceding stage of the production of the bottled goods. Moreover, because heat is generated in the first instance in the adhesive itself, the adhesive can be activated without any heat being applied directly to the cap or bottle, thereby avoiding distortion of the cap which is usually made of a plastic such as polyvinyl chloride and the plastics bottle.
- 30 The frequency of the alternating magnetic field used for the heating operation may be from 0.5 to 100 megacycles/second or higher, but will usually be 15 to 30 megacycles/second. Any suitable source of sufficient power output can be employed, typical sources have power outputs of 0.1 to 30 Kw, but an output of 2 to 5 Kw will generally be most suitable. It is preferred to choose the frequency and field strength in accordance with the size and shape of the workpiece and the composition of the adhesive, so as to give an effective heating time of 2 minutes or less, usually a few seconds.
- 35 Apparatus which can be used for carrying out the process of the invention is illustrated diagrammatically in the accompanying drawing, and consists of a generator 1 connected to a power supply 2, and an electrically operated timing device adapted to operate the generator so that the alternating field is applied to a work coil 4 for a predetermined and preset time. A typical generator has a rating of 5 Kw and operates at 27.12 megacycles per second. The work coil and its immediate surroundings are provided with cooling means, preferably a thermostatically controlled, closed circuit system 5 in which distilled water is used as the cooling medium. (Less pure water gives rise to greater energy losses in the cooling system, and may itself become heated sufficiently to destroy or reduce its effectiveness). Various mechanisms, indicated schematically at 6, may be used to transport the assembly to
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be bonded to the proper position within the work coil. The configuration of the work coil will be chosen so as to be suited to the shape and size of the assembly.

- 5 In an alternative method of working the work coil may be moved with respect to the assembly to be bonded.

The following Examples illustrate this invention; "parts" and proportions are by weight.

- 10 The words "Foliac", "Brabender", "Sternite" and "Dixie" are Registered Trade Marks.

**EXAMPLE 1**

57 parts of graphite in the form of platelets (Foliac Graphite, Large Flake 1A manufactured by Graphite Products Limited) were blended with 43 parts of polypropylene (GSE 108 manufactured by I.C.I. Limited) on a Brabender plastograph with a mixing head attachment. A sheet 0.51 mm. thick of the resulting composition was compression moulded at 200°C. A sample cut from this sheet was placed between two strips of polypropylene 12.7 mm. wide and 6.3 mm. thick to give a lap joint with 12.7 mm. overlap. The assembly 25 was then held together under contact pressure and placed in a 4 turn barrel coil connected across the output of a 1.2 Kw induction generator operating at 27.12 megacycles per second. Powder was supplied to the work coil 30 for 10 seconds at an anode current of 0.2 amps (this is an approximate measure of the power level), during which time the polypropylene containing the graphite particles was heated to a sufficiently high temperature to melt it and the surface of the polypropylene bars in contact with it. The assembly was allowed to cool for one minute before removing it from the work coil. The bonded assembly was then mounted in a Hounsfield Tensometer and the 35 strength of the lap joint was determined at a cross head separation speed of 2.5 cm. per minute. A lap shear strength of 7 kg./sq. cm. was obtained.

**EXAMPLE 2**

30 parts of the graphite used in Example 1 was blended with 70 parts of a high impact polystyrene (Sternite 122 manufactured by Sterling Moulding Materials Limited). A gasket was moulded from this composition and placed between the body and lid of a polystyrene battery case. The case was placed within the confines of a rectangular single turn work coil so that the adhesive composition was in close proximity to the coil. The work coil was connected to the output of a 5 Kw induction generator operating at 27.12 megacycles per second. Power was supplied to the work coil for 30 seconds at an anode current of 0.3 amps. At the end of this period a bond had been formed between the lid and body of the battery case.

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**EXAMPLE 3**

Compositions were prepared containing 10, 20, 40 and 57 percent respectively of an amorphous particulate carbon (Dixie Carbon Black 70 ISAF manufactured by Anchor Chemical Company) in the polypropylene of Example 1. Discs 31.7 mm. in diameter and 2.0 mm. thick were compression moulded from each of these compositions. The discs were placed in turn inside a holder made from polytetrafluoroethylene in a two-turn barrel coil connected as in Example 1. Power was supplied to the coil for 60 seconds at an anode current of 0.3 amps. The temperature of each disc immediately after the power had been switched off was measured by placing a thermocouple lightly in contact with one surface of the disc. The table below gives the increase in temperature of the disc above ambient temperature together with the volume resistivity of the respective compositions as measured by British Standard No. 2784 method 202B with metal foil electrodes.

TABLE

| Weight Percent Carbon | Temperature Rise | Resistivity<br>( $\log_{10}$ ohm. cm.) |
|-----------------------|------------------|--|
| 10                    | 4                | Greater than 7                         |
| 20                    | 18               | 4.0 — 4.3                              |
| 40                    | 49               | 2.8 — 3.1                              |
| 57                    | 75               | 2.1 — 2.5                              |

57 parts of graphite in the form of approximately spherical particles (S.4505 graphite manufactured by the Anchor Chemical Company) was blended with 43 parts of the same

polypropylene as was used in Example 1. A sheet 1.3 mm. thick was compression moulded from this composition. A sample cut from this sheet was placed in a two-turn barrel coil con-

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ected as in Example 2. Power was supplied to the coil at an anode current of 0.5 amps. The composition melted after 100 seconds.

Although in Examples 1 and 2 the adhesive composition is based on a thermoplastic polymer of similar nature to the surfaces to be bonded, it will be understood that the process of the invention can be applied also when one or both of the said surfaces are different in nature from the adhesive material. Naturally the adhesive chosen in any particular case will be one which has suitable affinity for, or is known to be suitable for use with, the particular surfaces which are to be joined. The determination of a suitable adhesive for any particular purpose will be easy for a skilled worker. Example 3 shows the relation between the resistivity of the carbon-containing adhesive and the rate at which the composition is heated using a constant power input to the generator, while Example 4 shows that amorphous carbon can be used in place of the graphite of Example 1.

The use of carbon particles has several advantages over the use of ferro-magnetic particles in a similar way. Thus it is found that they have a much smaller tendency to separate out under gravity when the composition melts, and thus remain more uniformly distributed and in general appear at the surface of the adhesive layer to a smaller extent; for a similar reason their use in initially liquid compositions is attended with less difficulty as the result of settling. Carbon is also found to be substantially free from the tendency to cause degradation or decomposition of the material of the adhesive which characterises some ferro-magnetic metals; moreover it is not subject to

corrosion. Finally carbon particles are much less abrasive in mixing machinery and other devices used to make the adhesive composition.

#### WHAT WE CLAIM IS:—

1. A method for effecting adhesion between two articles which comprises interposing between them, and in contact with a surface of each, a thermally activatable adhesive composition containing carbon particles, and subjecting the assembly of articles to be bonded to the action of a high frequency alternating magnetic field until the adhesive composition has been heated sufficiently to become activated.
2. A method according to claim 1, wherein the carbon particles have an average diameter of 50—200 microns.
3. A method according to claim 1 or 2, wherein the surfaces of the articles to be joined are of the same or different polymeric materials.
4. A method according to claim 3, wherein one article is the neck of a plastics bottle and the other a plastics closure cap for the bottle.
5. A method according to claim 1, substantially as herein described with reference to any one of the Examples.
6. Articles bonded together by a method claimed in any one of claims 1—3 and 5.
7. Capped plastics bottles whose cap is bonded to the neck of the bottle by the method claimed in claim 4.

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1267198 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of  
the Original on a reduced scale*

